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⑦① Applicant: **BP Chemicals Limited**
Belgrave House 76 Buckingham Palace Road
London, SW1W 0SU(GB)

⑦② Inventor: **Adur, Ashok Mohan**
106 Carter Terrace
Hackettstown New Jersey 07840(US)
Inventor: **Anzini, David Joseph**
5610 South Geneva Road
Sodus New York 14551(US)
Inventor: **Shedd, Charles Dains**
3406 Lakefield Boulevard
Sugar Lane Texas 77479(US)

⑦④ Representative: **Hymers, Ronald Robson et al**
BP INTERNATIONAL LIMITED Patents
Division Chertsey Road
Sunbury-on-Thames Middlesex, TW16
7LN(GB)

⑤④ **Filled elastomer blends.**

⑤⑦ A halogen-free filled elastomer blend composition, containing at least two elastomers from the group: elastomeric ethylene-propylene copolymers and terpolymers, polyamide elastomers, elastomeric polyesters, isobutylene polymers, polyurethane elastomers, acrylic elastomers, natural rubber, polybutadiene and polyisoprene, as minor components, and a flame-retardant halogen-free inorganic filler as the major component.

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FILLED ELASTOMER BLENDS

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

5 The present invention relates to halogen-free filled elastomer blend compositions which are flame retardant and contain an inorganic filler in an amount which is at least 50% of the combined weight of filler and elastomer.

10 2. DESCRIPTION OF THE PRIOR ART

An "elastomer" is a rubber-like polymer which can be stretched to at least twice its original length and which retracts very rapidly to approximately its original length when the force exerting the stretching is released. An elastomer has an elastic modulus of about 10,000 psi (68.95 MPa) or less and an elongation usually greater than 200% in the uncrosslinked state at room temperature using the method of ASTM D638-72.

A "thermoplastic" material is a linear or branched polymer which can be repeatedly softened and made flowable when heated and returned to a hard state when cooled to room temperature. It generally has an elastic modulus greater than 10,000 psi (68.95 MPa) using the method of ASTM D638-72. In addition, thermoplastics can be molded or extruded into articles of any predetermined shape when heated to the softened state.

A "thermoset" or vulcanisate is a crosslinked polymer which when subjected to heat does not flow or soften.

25 The term "filler" is used for additives such as organic or inorganic materials which reduce the cost of a composition and may also provide additional characteristics such as imparting fire or flame retardance, stiffening the composition or other such improvements.

Thermoplastic elastomers (TPEs) are a family of materials that have the properties of elastomers but can be processed like thermoplastics. TPEs are generally made by special block copolymerisation or graft polymerization or blending of two polymers. In each case the thermoplastic elastomer contains at least two segments, one of which is thermoplastic and the other elastomeric.

An example of a block copolymerised TPE is disclosed in U.S. Patent 3,792,127 which discloses the block copolymerisation of styrene and butadiene. The TPE consists of polystyrene blocks and polybutadiene blocks. By itself, polystyrene is a thermoplastic while polybutadiene is an elastomer. Similarly, 35 TPEs can be made by graft polymerization as in U.S. Patent 3,265,765 to Holden et al and in the article by Hartman et al "Butyl Grafted to Polyethylene Yields Thermoplastic Elastomer", Rubber World, pages 59 to 64, October 1970, which discloses thermoplastic elastomers made by grafting an elastomeric segment, polyisobutyl to a thermoplastic material, polyethylene.

Other examples of a blend of a thermoplastic and an elastomer to produce a TPE are disclosed in U.S. Patent 4,130,535 to Coran and U.S. Patent 3,806,558.

40 The use of fillers in small amounts of less than about 40% by weight, such as talc, mica, titanium dioxide, calcium carbonate, aluminum hydroxide, to reduce the cost or to add rigidity to a product is well known. For example, U.S. Patent 3,965,055 to Shichman et al discloses a vulcanisate prepared from a rubber-resin blend wherein the resin particles are dispersed in the rubber. Other modifying or compounding ingredients such as carbon black, clays, hydrated silica and the like, may be incorporated into the rubber and resin, if desired. However, the composition results in a vulcanisate which by definition is not a thermoplastic but rather a thermoset.

45 U.S. Patent 4,327,199 to Coran et al discloses thermoplastic compositions comprising neutralized acid-containing acrylic copolymer rubber obtained by blending thermoplastic crystalline polyester therewith. The properties of this composition can be modified with the addition of other ingredients such as carbon black, silica, titanium dioxide, pigments, clay and the like. Typical additions of filler can vary from about 15-80 parts by weight of filler per 100 parts by weight of rubber. Thus, the filler is a minor portion (13-44%) of the total composition.

Some fillers, such as antimony trioxide and chlorinated or brominated compounds are used to impart additional properties such as fire retardance. For example, U.S. Patent 4,275,180 to Clarke discloses a

crosslinkable or crosslinked blend of an elastomer and a thermoplastic polymer, such that both the elastomer and the thermoplastic polymer are substantially free of halogen-containing substances. However, all of Clarke's examples include either chlorinated or brominated compounds. Hence the total composition contains halogen-containing compounds which generate hydrochloric acid gas and other toxic and harmful vapors when subjected to high heat and/or an open flame. These vapors make the composition unsuitable for applications in enclosed spaces such as high rise buildings and military and aerospace vehicles. Moreover, Clarke's blend contains only minor amounts of filler, usually not more than 40% by weight.

U.S. Patent 4,108,962 to Pedlow discloses flame retardant external tape coverings that are used for covering polyolefin insulating material. The resinous base substance of the tape composition can be a halogen-containing thermoplastic.

SUMMARY OF THE INVENTION

The present invention relates to a halogen-free thermoplastic elastomer composition, comprising: (A) a flame-retardant halogen-free inorganic filler and (B) at least two elastomers selected from the following group:

elastomeric ethylene-propylene copolymers and terpolymers, polyamide elastomers, elastomeric polyesters, isobutylene polymers, polyurethane elastomers, acrylic elastomers, natural rubber, polybutadiene and polyisoprene, or a graft copolymer or block copolymer comprising polymer segments of at least two such elastomers in which composition the weight % of (A) is at least 50% of the total weight of (A) and (B).

Preferably antioxidants, release agents, carbon black and other additives included in the composition as minor additives, cumulatively do not exceed 15% by weight of the total composition.

The composition can optionally be made partially crosslinked by methods normally used to dynamically cure thermoplastic elastomers. The composition can also be made highly or completely crosslinked by known methods after molding or extrusion into its final shape.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with a preferred embodiment of the present invention, a halogen-free thermoplastic elastomer composition comprises at least two elastomers as minor components, which cumulatively occupy less than 50% by weight of the total composition and a flame-retardant halogen-free inorganic filler as the major component, and a curing agent. It is important to note that this composition does not include a conventional thermoplastic polymer such as polypropylene or polystyrene. However, the composition has the following characteristics:

1. low-smoke containing only small quantities of hazardous gases;
2. flame retardance;
3. thermoplastic-like processability; and
4. exceptional mechanical properties.

The halogen-free inorganic filler, which is the major component of the composition can include hydrated magnesia, aluminium trihydrate, hydrated calcium silicate, clays, talcs, carbonates, hydrates, oxides, other silicates, nitrogen/phosphorous containing additives which give off non-hazardous gases and/or low smoke as well as other suitable filler materials listed in Rubber World Magazine Blue Book at pages 253-263 (Lippincott and Peto 1984), which is incorporated by reference herein.

One or more fillers can be used in the composition to provide the combination of properties desired for each specific application.

When aluminium trihydrate or hydrated magnesia is used as the filler, the thermoplastic elastomer composition of the present invention has a high limiting oxygen index (LOI), and also burns with substantially no visible smoke. The combination of low smoke generation and resistance to burning are very desirable properties for many applications such as insulating cables with low smoke and flame retardant jacketing, useful in building construction and in military vehicles.

Nitrogen/phosphorus additives such as Char-Guard 329 marketed by Great Lakes Chemical Corporation act in the condensed phase to form a protective intumescent char when exposed to a flame. (Char-Guard is a registered trade mark). This char provides excellent protection against long or repeated exposure to an ignition source, and virtually eliminates dripping problems often encountered. Low total nitrogen/phosphorus additive levels provide excellent protection during flammability testing while maintaining excellent mechanical and electrical properties. Char-Guard 329 is stable under processing conditions, does not migrate from

the polymer, and produces polymer systems with very low specific gravity.

The preferred elastomers for use in the present invention include: elastomeric ethylene-propylene copolymers and terpolymers, polyamide elastomers, elastomeric polyesters, isobutylene polymers, polyurethane elastomers, acrylic elastomers, natural rubber, polybutadiene, polyisoprene, and other elastomers (sometimes called rubbers) which satisfy the following additional requirements:

1. elastic modulus of 10,000 psi (68.94MPa) or less at room temperature when measured in the uncrosslinked state as per ASTM D638-72;
2. halogen content less than 0.01% by weight; and
3. do not emit hazardous gases such as hydrogen cyanide or carbon monoxide above 0.1% by weight, when heated.

Although it is preferable to use two or more elastomers to get the right combination of end use properties, in some cases one elastomer can provide the necessary performance characteristics by virtue of being a block copolymer or graft copolymer containing two of the polymer segments normally present in two separate elastomers. An example of such elastomer is polyester elastomer grafted polybutadiene.

The relative proportions of the two elastomers vary over a wide range to achieve the desired mechanical properties and extendability, which is a qualitative measure of thermoplasticity. The preferred ratios for each elastomer combination depend on such criteria as the "green strength" of the two elastomers, the ratio of tensile modulus of the two elastomers, the solubility parameter of the two elastomers, and extent of curing or crosslinking.

The ratio of selected elastomers can vary from about 95:5 to 30:70 respectively, in parts by weight, while the preferred ratio can vary from about 95:5 to 50:50 respectively in parts by weight.

The proportion of the filler such as clay or mica or aluminium trihydrate can range from about 50 to 90% preferably about 50-75% by weight of filler in the filled elastomer blend composition. In certain cases it may be advantageous to include two or more fillers, some of which can impart low-smoke characteristics, and other properties.

The curing system used to accomplish partial or complete cross-linking of the filled elastomer composition can comprise organic peroxides, sulfur, metal alkylates, epoxies, amines, azides, phenolic resin curing agents, metal oxides, quinone derivatives and the like.

The particular type of curing agent used depends upon the specific cure site in the polymer and the properties desired in the finished product. Specific examples are disclosed in US Patent 3,284,421 to Breslow and US Patent 3,297,674 to Breslow et al. Other suitable curing agents are disclosed in the Encyclopedia of Chemical Technology, Volume 17, Second Edition, (Interscience Publishers, 1968), Science and Technology of Rubber, edited by F.R. Eirich, Chapter 7, pp 291-335 (Academic Press, 1978), Rubber Technology, edited by Maurice Morton, Chapter 2, pp 19-50 (Van Nostrand Reinhold, 2nd edition 1973) and Organic Peroxides, Volume 1, Daniel Severn, (Wiley Interscience), 1970, and in US Reissue Patent 31,518 to Fischer at column 3, line 26 to column 4, line 35, the disclosure of which is incorporated by reference herein.

In general, the amount of elastomeric curing agent used will depend upon the extent of thermoplasticity desired in the elastomer composition. To obtain a partial cure, the curing agent can vary from about 1-90%, preferably about 5-75% and more preferably about 10-40% of the amount necessary for a substantially complete cure or crosslinking. The exact amount of elastomer curing agent is determined by the formulator taking into consideration such factors as the final method of fabricating the elastomer and the balance of properties desired for its end use.

In using the limited amount of curing agents or curatives, the mixing temperature of the blend containing the curing agent, the filler and elastomers is selected so that whatever amount of curing agent is employed, it is substantially consumed during the reaction.

A filler-elastomer composition which has the desired degree of improvement in resistance to deformation at elevated temperature and is still processable as a thermoplastic would be considered to have an adequate amount of curing agent.

As a practical rule of thumb, the effective activation temperature for the curing agent may be taken as the temperature at which at least 95% of the curative has been decomposed to yield free radicals within a 0.5 minute time period. It is preferable to select a curative having an activation temperature above the softening point of the filled elastomer composition.

It is also possible to use a curing agent having an activation temperature at or below the softening point of the filled composition. The activation temperature would ordinarily be above 240°F, (116°C) preferably about 300°F (149°C).

The maximum activation temperature would ordinarily not be more than 450°F, (232°C) preferably not greater than 400°F (204°C). The data on the common peroxide curatives, such as 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane ("Peroxide I") and dicumyl peroxide ("Peroxide II") is given in the following table.

<u>Half life in Toluene</u>			
Temperature		Peroxide I	Peroxide II
°F	(°C)		
240	(116)	21 hours	10.2 hours
270	(132)	2 hours	1.75 hours
335	(168)	ca. 5 minutes	ca. 3 minutes
360	(182)	47 seconds	22 seconds
390	(199)	7.2 seconds	3.6 seconds

In contrast to the half-life data tabulated above, at 360°F, (182°C) the time to reach about 95% decomposition for Peroxide I and Peroxide II is approximately 4 minutes and 1½ minutes, respectively.

The dynamic partial cross-linking treatment substantially exhausts the action of the curing agent so that there is little or no tendency for further advancement of cure to take place subsequently. It is also desirable to further insure termination of the action of any remaining cross-linking agent, by adding to the mix, at the end of the dynamic partial curing step, a small amount of free-radical scavenging agent, such as a stabiliser or antioxidant.

Such stabiliser may be added and mixed in for the last minute or so of mastication. The dynamically partially cured material may be subjected to one or more "refining" passes on a mill, and the stabilizer or antioxidant can be added in the course of or just prior to refining.

A complete cure which would change the characteristics of the composition to one that is non-thermoplastic, but thermoset in nature would be an additional part of this invention. In this case the thermoplastic composition would be moulded or extruded into final shape and form and then the curing agent would be activated to convert it to a thermoset.

The elastomeric curing agent can be used alone or in combination with auxiliary substances, such as accelerators, activators, stabilisers, free radical scavenging agents, chain extenders and antioxidants. Such materials, for example include aldol alpha-naphthylamine, 2,2,4-trimethyl-1,1,2-dihydroquinoline, diphenylamine acetone condensate, octylated diphenylamine, N-phenyl-N'-cyclohexyl-p-phenylene diamine, 2,6-di-tert-butyl-4-methyl phenol, styrene-resorcinol resin, o-cresol monosulfide, di-p-cresol-2-propane, 2,5-di-tert-amyl hydroquinone, dilauryl-3,3'-thiodipropionate and similar dialkyl thiodipropionates. Colouring agents such as carbon black can also be used.

Other suitable additives are listed in Rubber: Natural and Synthetic, Stern, (Palmerton Publishing Company, New York, 1967), especially at pages 244-256; and also Chemistry and Technology of Rubber, Davis and Blake (Reinhold, New York, 1937).

The partial cure of the filled elastomeric blend is accomplished by contacting the blend with amounts of the curing or crosslinking agent that are insufficient for a substantially crosslinked cure.

In addition to insuring that the amount of elastomeric curing or crosslinking agent is less than the amount necessary to effect a full cure or crosslinking, parameters such as the curing temperature, and time of cure are also carefully controlled to insure full activation of the curing agent present in the blend. More than one curing agent can also be used.

The curing temperatures for the filled elastomeric blend can vary from about 160-400°F (71 to 204°C), preferably 220-400°F, (104 to 204°C) and most preferably 320-400°F (160 to 204°C). The curing temperatures are limited by the stability of the specific elastomers used in the blend. For example, filled blends of acrylic elastomers with polyester elastomers cannot be processed at temperatures above about 400°F, (204°C) or below about 320°F (160°C). At temperatures above 400°F, (204°C) the acrylate degrades and gives off decomposition gases. At temperatures below about 320°F (160°C) the polyester elastomer cannot be processed because it is close to the melting point of the polymer.

Typical cure times can vary from about 1 to 30 minutes, preferably about 3 to 20 minutes, depending

upon the cure system and temperature utilised. Naturally, the time required for the dynamic partial cure will vary with such parameters as the particular copolymers employed in the blend, the kind and amount of curative, and the temperature at which the partial cure is carried out.

To best accomplish the dynamic partial cure, the filler, the elastomers and cure system can be contacted on an open roll mix, or in an internal mixer such as a Banbury mixer, or an extruder-mixer or a transfer mixer.

A convenient method of accomplishing the blending is to premix the ingredients and then extrude the blend composition through a heated extruder. Other mixing means, such as a Brabender mixer, a Banbury mixer, roll mills and the like may also be employed for the process. Since curing agents provide some crosslinking at elevated temperatures, it is not necessary to carry out the reaction in a closed vessel. A conventional single or multiple screw extruder accomplishes blending without the use of auxiliary equipment and for this reason is a particularly desirable reaction vessel. Other pieces of equipment suitable include the gelmat mixer, kneader-extruder, continuous and batch mixers.

Optionally, monomers in small quantities can be introduced to provide increased cure levels if necessary, by forming some graft or cografted polymers. In any case, irrespective of the equipment used, the blended products can be recovered by any method or system which separates or utilises the "filled elastomer blend" includes recovery of the composition in the form of precipitated fluff, pellets, powders and the like, as well as further blended pellets, powders and the like or in the form of shaped articles formed directly from the resulting filled elastomer blend.

The processability of the filled elastomer blend can be assessed for different applications by examining test specimens for surface finish smoothness that is substantially free from obvious imperfections. A non-thermoplastic material has an irregular grain and poor definition as well as lack of sharpness. Although these criteria are qualitative, those skilled in the art are readily able to ascertain satisfactory products from those that are unsatisfactory by visual examination and touch.

The processability of the inventive blends can be evaluated by subjecting samples of the blend to such shaping operations as extrusion, injection moulding or compression moulding.

Extrusion is the shaping method of choice where long continuous forms, such as hose, window seals, wire coatings, flat sheets, and the like are desired. It is important that the extruded articles have acceptable surface smoothness. Extrudability can be evaluated in accordance with ASTM D2230.

For satisfactory injection moulding, the filled elastomer blend must form a homogeneous article of uniform strength in the mould. The flow viscosity characteristics of such elastomeric blends are adequate to insure filling the mould properly under the operation conditions.

The elastomeric nature of objects shaped from the thermoplastic blend of the present invention can be demonstrated by a low elongation set at break, measured in accordance with ASTM D-412.

The thermoplastic nature of the inventive blends can be demonstrated by their reprocessability, especially after repeated extrusion with retention of desirable characteristics.

In processing the inventive blend, it can be advantageous to include a release agent or lubricant, particularly from the standpoint of improving the extrusion quality of the blend composition. For this purpose, any known lubricant conventionally used in rubber or plastics processing can be used, generally in amounts varying from about 0.2 to 3 parts by weight, preferably about 0.5 to 1 part by weight per 100 parts of the elastomers in the filled blend.

In addition, all blends preferably contain stabiliser packages. The amount of stabiliser system can vary from about 0.5 to 5 parts by weight, and more preferably about 1 to 3 parts by weight of the thermoplastic composition. The types and amounts of the stabilisers in the stabiliser system would depend on the specific elastomer and the end use of the filled blend.

For example, in a typical blend of hydrated magnesia, an acrylic elastomer and an ethylene-propylene-diene elastomer, a stabiliser system containing 0.2% of a hindered phenol antioxidant such as Cyanox 1790 from American Cyanamid, 0.2% calcium stearate and 0.2% of a phosphite secondary antioxidant such as Irgaphos 168 from Ciba Geigy is used. If, in addition, the end use application involved outdoor exposure, an ultraviolet stabiliser such as 0.3% of a hindered amine like Hostavin N20 from American Hoechst is used. All these weight percentages are based on the weight of the elastomers.

In another typical blend of hydrated alumina, an acrylic elastomer and a polyester elastomer, it has been found that the use of a three component stabiliser system is uniquely suitable in obtaining a desirable product. The first component of the stabiliser system comprises a high molecular weight multi-functional sterically hindered phenol such as tetrakis [methylene 3-(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate] methane, more simply referred to as "tetrakis methane", available from Ciba Geigy Corp, as Irganox 1010. (Irganox is a registered trade mark). The high molecular weight multi-functional sterically hindered phenol functions as an antioxidant and thermal stabiliser.

The second component of the stabiliser system is an alkyl ester of a thiodipropionic acid such as dilauryl thiodipropionate ("DLTDP"), which functions as a secondary antioxidant.

The third component of the stabiliser system is a substituted benzotriazole and functions in the stabiliser system to protect the elastomeric blend against ultraviolet radiation.

5 Alternatively, Naugard 455 available from Uniroyal Co. can be used as part of a stabiliser system. These stabiliser systems are illustrative examples only and by no means restrictive. In fact, any suitable stabiliser system commonly known to one skilled in the art of stabilising polymers can be used.

The elastomeric blend of the present invention can be manufactured in a single operation, or in a number of operational steps.

10 In the single step operation, the filler, elastomers and curing agent are charged at the desired ratio to a suitable mixer such as Banbury internal mixer, transfer type extruder-mixer, extruder or any device that will enable efficient mastication of the blend at the desired temperature. The blending apparatus can be preheated to reduce the time necessary to reach the processing temperature range.

The blend is then held at the processing temperature while continuing the mixing for a time sufficient to 15 insure that effective partial cure of the blend has been accomplished.

During processing, the stabiliser system is then contacted with the blend and processing is continued for a short time, usually for about one minute or more in order to thoroughly incorporate the stabiliser in the blend and for the purpose of deactivating any residual curing agent.

20 In the multi-step process, the selected elastomer and curing agent are charged to a suitable apparatus wherein partial curing takes place. Thereafter, the partially cured elastomer is blended with the other selected elastomer, the filler, and other components as needed.

As previously stated, the polymer compositions are halogen free, thus decreasing the possibility of evolution of HCl, HBr or other toxic gases. In addition, the blends of this invention can include additional additives, for example, stabilisers, antioxidants, radical scavengers, ultraviolet stabilisers anti-hydrolysis 25 stabilisers, acid acceptors, colorants and pigments, preferably in amounts of not more than 15% and more preferably not more than 10% by weight.

An alternate method of crosslinking the compositions of the present invention is by using high energy, microwave or ultraviolet radiation. Radiation dose levels to achieve complete curing may range from 2 to 100 Mrads or more but a dose of 4 to 60 Mrads is preferable. For partial crosslinking, a dose of 0.5 to 10 30 may be effective depending on the specific elastomers in the blend.

In some cases, it may be desirable to add to the cross-linkable polymer composition a co-agent to assist in the crosslinking reaction. Such co-agents usually contain multiple unsaturated groups such as alkyl or acrylic esters. While their mode of action is not known with certainty, it is believed that they react with the initial radical formed on the polymer backbone to form a more stable radical, which undergoes coupling 35 reactions to form crosslinks more readily than chain scission reaction.

The co-agent can be for example, N,N'-m(phenylene)-dimaleimide, trimethylolpropane trimethylacrylate, tetraallyloxyethane, triallyl cyanurate, triallyl isocyanurate, tetramethylene acrylate, or polyethylene oxide glycol dimethacrylate. The amount of the co-agent is preferably up to about 5 parts by weight per 100 parts of the elastomer composition and preferably from 1 to 3 parts by weight per 100 parts 40 of the elastomer blend.

Filled elastomer blends according to the present invention can be used in a wide range of applications, and the preferred compositions find particular applications where resistance to hydrocarbon fluids and thermal aging is required. Thus, the compositions may be used as jacketing materials for wire and cable and as harnessing materials, particularly in automotive, military and aerospace applications, as well as 45 paneling and sheets in elevator shafts, marine or aerospace vessels, high rise buildings and other confined spaces where toxic smoke is a possible hazard in the case of a fire.

The blend compositions of the present invention have a unique combination of the following performance characteristics:

1. when exposed to a flame, only small amounts of hazardous gases are evolved and little or no 50 smoke is observed;
2. flame-retardance;
3. thermoplastic-like processibility even though the compositions comprise fillers and elastomers and may not contain conventional thermoplastics such as polyethylene, polypropylene and polystyrene;
4. exceptional mechanical properties especially tensile and tear properties.

55 In the following non-restrictive examples, which serve to illustrate the present invention, all percentages are by weight of the elastomer and filler taken as 100% unless otherwise indicated. Other additives such as curing agent, release agent, carbon black, stabilisers, antioxidants and the like are expressed as based on the weight of the filled elastomer blend.

The objective of the following examples is to show formulations which are thermoplastic, i.e mouldable and extrudable into good quality tapes, plaques, strips, wire and other articles, and to possess most if not all of the following minimum properties simultaneously:

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	<u>Property</u>	<u>Test</u>	<u>Value</u>
10	1. Tensile Strength	ASTM D-412	> 1000 psi (6.89 MPa)
	2. Elongation at break	ASTM D-412	> 130%
	3. Tear Strength	ASTM D-470	> 30 lbs/in (52 N/cm)
15	4. Hardness (Shore A)	ASTM D-2240	> 75A
	5. Limiting Oxygen Index	ASTM D-2863	> 30%
	6. Smoke Test	ASTM D-2863	Little or no smoke
20	7. Gas Analysis of Smoke	*	Low hazardous gases gases conc.
	8. Halogen Content based on total formulation of blend	by calculation	< 0.1%
25	9. Moldability using compression moulding	visual	good surface quality
30	10. Extrudability using a laboratory extruder	visual	good extrudability
35	11. Smoke Generation Test - Average of Smoke Optical Density of Smoke Generation	ASTM E662-83	< 160

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* Test Number 7 (gas analysis of smoke) was carried out using Draeger colorimetric tubes. Total of hazardous gases (HCN, NO_x, SO₂, H₂S, HCl, HBr, HF and total hydrocarbons) should not exceed 100 ppm in the flaming mode and 30 ppm in the non-flaming mode. For carbon monoxide, the criteria used was a maximum of 1000 ppm in the flaming mode and 300 ppm in the non-flaming mode.

Example 1 (Comparativ Example)

A composition was blended according to Example 1 of U.S. Patent 4,275,180 to Clarke, using the following ingredients and the procedure stated in column 7 of the patent:

<u>Ingredient</u>	<u>Parts by Weight</u>	<u>% Weight*</u>
Ethylene-methyl acrylate	123	57.75
elastomer		
Carbon black	21	-
Antimony Trioxide	15	7.04
Dechlorane Plus 25	15	7.04
(chlorinated flame retardant)		
Octadecyl amine (same release agent as Crodamine IHT)	3	-
Triallyl cyanurate	4	-
Block copolyester	60	28.17
Total	241	100.00

* % Weight does not include curing agent, carbon black, stabilisers and release agents.

After preparation, the composition was extruded and then irradiated with a dose of 12 Mrads and tested for mechanical properties and smoke analysis. The following results were obtained:

Halogen content:	5.16%
Tensile strength:	1798 psi (12.4MPa)
Elongation at break:	500%
Tear strength:	50.3 lb/in (88.1 N/cm)
Hardness (Shore A):	72A
Limiting Oxygen Index:	22%

<u>Smoke Gas Analysis:</u>	<u>Gas</u>	<u>Flaming</u>	<u>Non-flaming</u>
(values in ppm)			
	HCN	26.0	14.8
	NO _x	41.2	8.0
	SO ₂	25.0	1.3
	H ₂ S	0.8	0.2
	HCl	31.2	20.3
	HBr	-	-
	HF	6.0	0.1
Total of hazardous gases		130.0	44.7
	CO	1068.0	719.0
Smoke Generation Test:	Flaming	227	
	Nonflaming	281	
	Average	254	

The formulation of this example is outside the present invention because this formulation has low filler content (14%), high halogen content (5.16%), low L.O.I. (22%), and high hazardous gas evolution when burned.

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Example 2 (Comparative Example)

A composition using the formulation of Example 3 of U.S. Patent 4,275,180 was prepared in a laboratory Banbury internal mixer using the formulation and procedure listed in that example.

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<u>Ingredient</u>	<u>Parts by Weight</u>	<u>% Weight*</u>
Ethylene acrylic elastomer	30	31.9
used in Example 1		
Carbon black	2	-
Antimony Trioxide	6	6.4
Decabromodiphenyl Ether	12	12.8
Octadecyl Amine (same release agent as Crodamine IHT)	0.375	-
Triallyl cyanurate	1	-
Irganox 1010	0.375	-
Calcium carbonate	16	17.0
Hytrel thermoplastic elastomer	30	31.9
used in Example 3 of the above patent		
Stabilizer	2.25	
* % weight does not include curing agent, carbon black, stabilisers and release agents.		

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The mix was put on a rubber mill and compression moulded plaques were made and irradiated at 12 Mrads. The following results were obtained:

Halogen content: 10.25%

Tensile strength: 1658 psi (11.4 MPa)

Elongation at break: 5.75%

Tear strength: 52.0 lb/in (91.1 N/cm)

Shore Hardness: 84A

Limiting Oxygen Index: 21%

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Smoke Gas Analysis:		<u>Gas</u>	<u>Flaming</u>	<u>Nonflaming</u>
(values in ppm)				
5		HCN	8.5	12.0
		NO _x	35	8.0
		SO ₂	0.0	0.0
10		H ₂ S	0.6	0.0
		Hydrocarbons	95.0	125.0
		HCl	2.5	5.7
		HBr	88.5	35.0
15		HF	<u>1.7</u>	<u>0.2</u>
		Total hazardous gases	231.8	185.9
		CO	871.0	444.0
20	Smoke Generation Test:	Flaming	147	
		Nonflaming	167	
		Average	157	

25 The formulation of this example is outside the present invention because this formulation has low filler content (36.2%), high halogen content (10.25%), low L.O.I. (21%), and high hazardous gas evolution when burned.

30 Example 3

A filled elastomer blend was prepared using the following ingredients (all weights are in percentages and do not include stabiliser, release agent, carbon black or curing agents).

35	<u>Component</u>	<u>Weight %</u>
	(a) Aluminium trihydrate (ATH) of medium particle size 0.8mm and BET surface area 4 m ² /g	52.9
40	(b) Ethylene-methyl acrylate elastomers containing 20% silica and having elongation of 6.40% and a Mooney viscosity of 30ML (H-4) at 212°F	33.5
45	(c) Segmented copolyester elastomer with a specific gravity of 1.18, hardness of 40D and elongation of 170%	13.6
50	Total	<u>100.0</u>

55 The blend was prepared in a laboratory Banbury and also contained 2.63 weight per cent carbon black, 0.58 weight per cent vinyl silane, 0.39 weight per cent stabiliser package, and 1.74 weight per cent triallyl cyanurate. The stabiliser package consists of 1 part each of Irganox 1010 and Tinuvin 327 to 4 parts of DLTDP. This blend was then compression moulded into strips and extruded into tapes and then irradiated to 15 Mrads of ionizing radiation. The following results were obtained:

Test Tensile strength: 1904 psi (13.13 MPa)
 Elongation at Break: 200%
 Tear Strength: 47 lb/in (82.3N/cm)
 Shore Hardness: 89A
 5 Limiting Oxygen Index: 34%
 Smoke Test: Very little smoke
 Halogen Content: 0.0067%
 Smoke Generation Test: Flaming 37; Nonflaming 154; Average 95.5

10	Smoke Gas Analysis:	<u>Gas</u>	<u>Flaming</u>	<u>Nonflaming</u>
	(values in ppm)			
		HCN	6.2	4.0
15		NO _x	37.0	0.0
		SO ₂	0.0	0.0
		H ₂ S	0.7	0.0
20		Hydrocarbons	46.0	11.7
		HCl	2.7	3.3
		HBr	0.0	0.0
		HF	<u>0.1</u>	<u>0.1</u>
25		Total hazardous gases	92.7	19.1
		CO	875.0	269.0

30 Example 4

A filled elastomer blend containing the following components was prepared on a large Banbury (all weights in % and do not include carbon black, curing agent, stabilisers or release agent).

35	<u>Component</u>	<u>Weight %</u>
	(a) same aluminium trihydrate (ATH) used in Example 3	53.8
40	(b) same polyester elastomer used in Example 3	15.4
	(c) same ethylene acrylate rubber used in Example 3	<u>30.8</u>
	Total	100.0

45 The blend also contained 7.24% carbon black, 0.27% vinyl silane as release agent, 0.47% stabiliser package used in Example 3 and 0.15% VAROX peroxide from R.T. Vanderbilt Co. as curing agent.

The thermoplastic blend was compression moulded into strips and extruded into tapes for testing. The following results were obtained:

50

Test Extrudability: Excellent
 Tensile strength: 935 psi (6.4 MPa)
 Elongation at Break: 310%
 55 Tear Strength: 53 lb/in (92.8 N/cm)
 Shore Hardness: 78A
 Limiting Oxygen Index: 32%

TestSmok Test: No smok
 Halogen Content: 0.00786%
 Moldability: Excellent
 Smoke Generation Test: Flaming 153; Nonflaming 152; Average 152.5

5

Smoke Gas Analysis:		<u>Gas</u>	<u>Flaming</u>	<u>Nonflaming</u>
		(values in ppm)		
10		HCN	1.0	1.2
		NO _x	0.1	0.0
		SO ₂	0.0	0.0
		H ₂ S	0.7	3.3
15		Hydrocarbons	245.0	18.3
		HCl	3.8	2.5
		HBr	0.0	0.0
20		HF	<u>0.2</u>	<u>0.1</u>
		Total hazardous gases	256.8	25.4
		CO	767.0	208.0

25

Examples 5 and 6

Two blends were prepared using the same procedure as in Example 4 using slightly different ratios listed below. Weight percentages for (a), (b) and (c) total 100%. Other additives also in weight percentage of this total.

30

Example 5

35

<u>Component</u>	<u>Weight %</u>
(a) same (ATH) as in Example 3	50.26
(b) same polyester elastomer as in Example 3	14.37
40 (c) same acrylic rubber as in Example 3	<u>35.37</u>
Total	100.00%

45 The blend also contained 2.69% carbon black, 0.43% stabiliser package used in Example 3 and 0.29% VAROX peroxide curing agent.

When blended and tested the following results were obtained:

Tensile strength: 893 psi (6.16 MPa)
 Elongation at Break: 290%
 50 Tear Strength: 41.1 lb/in (72 N/cm)
 Extrudability: Excellent

55 TestLimiting Oxygen Index: 35%
 Smoke Test: No smoke
 Halogen Content: 0.00752%

Example 6

	<u>Component</u>	<u>Weight %</u>
5	(a) same (ATH) as in Example 3 above	53.63
	(b) same polyester elastomer as in Example 3	13.38
	(c) same acrylic rubber as in Example 3	<u>32.99</u>
10	Total	100.00%

The blend also contained 2.59% carbon black, 0.57% vinyl silane release agent, 0.40% stabiliser package used in Example 3 and 0.26% VAROX peroxide curing agent.

15 When blended and tested the following results were obtained:

Tensile strength: 1062 psi (7.32 MPa)

Elongation at Break: 270%

Tear Strength: 28.8 lb/in (50.4 N/cm)

Extrudability: Excellent

20 Limiting Oxygen -

Smoke Test: No smoke

Halogen Content: 0.00697%

25 Example 7

One blend was prepared using the same procedure as in Example 4 using a polyester elastomer with a hardness of 40D, specific gravity of 1.16 and elongation of 560%. The weight percentages are identical to those as in Example 5. The properties of the thermoplastic blend made from the filled elastomers are as follows:

30 Tensile strength: 622 psi (4.29 MPa)

% Elongation: 335%

Tear Strength: 42.6 lb/in (74.6 N/cm)

Extrudability: Excellent

35 Smoke Test: No smoke

Halogen Content: 0.00752%

40 Example 8

A blend identical to Example 6 was prepared except magnesium oxide was substituted for the ATH used in that example. The blend extruded with some difficulty but gave the following properties:

Halogen Content: 0.00697%

Tensile Strength: 2055 psi (14.17 MPa)

45 Elongation: 120%

Tear Strength: 35.5 lb/in (62.17 N/cm)

Limiting Oxygen Index: 31%

Shore Hardness: 93A

50 Smoke Test: No smoke, low toxicity

Example 9

55 A blend identical to Example 6 was prepared except an ethylene-propylene-hexadiene terpolymer elastomer was substituted for the ethylene-acrylate rubber. The following properties were observed with the thermoplastic blend.

Thermoplastic Extrudability Excellent

Tensile Strength 1091 psi (7.52MPa)

Elongation 130%
 Shore Hardness 90A
 Tear Strength 31 lb/in (54.29 N/cm)
 Smoke Test Low smoke, low toxicity
 5 Halogen Content 0.00697%

Example 10

10 A blend containing the following was prepared in a laboratory Banbury.

<u>Ingredient</u>	<u>Weight %</u>
Ethylene-acrylate rubber used in Example 3	30.8
15 Polyester elastomer used in Example 3	15.4
ATH used in Example 3	51.6
Talc	<u>2.2</u>
20 Total	100.0%

The blend also contained 7.6% carbon black, 0.27% vinyl silane release agent, 0.15% Varox curing agent and 0.46% stabiliser package used in Example 4.

25 When tested, the formulated filled elastomer blend extruded like a thermoplastic material and had the following properties:

Halogen Content 0.00767%
 Tensile Strength 1167 psi (8.05 MPa)
 Elongation at break 165%
 30 Tear Strength 45 lb/in (78.81 N/cm)
 Shore Hardness 79A
 Limiting Oxygen Index 31%
 Smoke Test No smoke
 Extrudability Excellent

35

Example 11

A blend similar to that in Example 4 was prepared in a laboratory Banbury but instead of the polyester elastomer used in that example, another polyester with hardness of 60 Shore D, 6100 psi tensile strength,
 40 400% elongation at break and a specific gravity of 1.24. The following properties were obtained:

Halogen Content: 0.00786%
 Tensile Strength 1129 psi (7.78 MPa)
 Elongation at break 190%
 45 Tear Strength 36 lb/in (63 N/cm)
 Shore Hardness 80A
 Limiting Oxygen Index 32%
 Smoke Test No smoke
 Extrudability Excellent

50

Example 12

A blend similar to that in Example 4 was prepared in a laboratory Banbury with two changes. The ATH used in that example was replaced with one that had a median particle size of 0.5 μm , a BET surface area of 7m²/g that had a surface-treatment of acrylic rubber. Further, the polyester elastomer was ground to a 20 mesh powder before introduction into the Banbury. The following properties of the filled elastomer blend resulted:

Halogen Content 0.00788%

Tensile Strength 1543 psi (10.64 MPa)
 Elongation at break 205%
 Tear Strength 31 lb/in (54.29 N/cm)
 Shore Hardness 84A
 5 Limiting Oxygen Index 32%
 Smoke Test No smoke
 Extrudability Excellent

10 Example 13

A blend similar to Example 4 was prepared except the acrylic rubber was replaced with an ethylene methyl acrylate copolymer with specific gravity 1.12, 1300% elongation at break and a Mooney viscosity of 29ML (1 + 4) at 212°F. The results obtained had the following properties:

15 Tensile Strength 1012 psi (6.98 MPa)
 Extrudability Excellent
 Elongation 170%
 Halogen Content 0.00786%
 Shore Hardness 84A
 20 Tear Strength 31 lb/in (54.29 N/cm)
 Smoke Test No smoke
 Limiting Oxygen Index 33%

25 Example 14

A blend was prepared according to the procedure in Example 3 but with the following components:

	<u>Component</u>	<u>Weight %</u>
30	ATH used in Example 12	52.5%
	Polyester elastomer used in Example 3	15.8%
	Acrylic elastomer used in Example 3	<u>31.7%</u>
35	Total	100 %

In addition the blend contained 7.44% carbon black, 0.28% vinyl silane release agent 0.31% stearic acid process aid, 0.15% Kemamine 990D release agent from Humko Products, 2.22% Nauguard 455 antioxidant from Uniroyal, 0.555% DLTDP secondary antioxidant 0.155% VAROX powder from R.T. Vanderbilt as curing agent, based on weight on 100% of total formulation listed above. The blend gave the

40 following properties upon extrusion into tape or compression moulded into plaques:
 Tensile Strength 1389 psi (9.58 MPa)
 Elongation 200%
 Extrudability Excellent
 45 Mouldability Excellent
 Tear Strength 40 lb/in (70.05 N/cm)
 Shore Hardness 84A
 Limiting Oxygen Index 34%
 Smoke Test No smoke
 50 Halogen Content 0.00%

Example 15

55 A blend made similar to Example 14 was prepared except that 52.5% of surface treated ATH was replaced with 50.3% of the same ATH and 2.2% of Emtall 500 talc. The following properties were obtained with this blend:

Tensile strength 1397 psi (9.63 MPa)

Elongation at break 245%
 Shore Hardness 84A
 Tear Strength 43 lb/in (75.3 N/cm)
 Limiting Oxygen Index 30%
 5 Extrudability Excellent
 Mouldability Excellent
 Smoke Test No smoke
 Halogen Content 0.00%

10

Example 16

The blend prepared in Example 4 was extruded onto a 360mil (9.14mm), O.D. wire using a 2½" diameter extruder and barrier screw with a 3:1 compression ratio. The cable jacketing had a thickness of 40 mil. and
 15 a draw ratio of 1.93:1. The melt temperature was 380°F (193°C).

Example 17

20 Blends prepared in Examples 4, 7, 15 were compression moulded into sheets 75 mil. (1.9mm) thick in a compression mould at a temperature of 400°F(204°C) and 30,000 psi (206.8MPa) pressure. The sheets can be used for paneling in aircraft or marine vessels.

25 Example 18

The blend prepared in Example 12 was dusted with 0.5 per cent of the following dusting agents: Emtall 500 from-Engelhard, Vertal talc from H.M. Royal, Mistron vapor FA 750 high density polyethylene powder from Cyprus Co., and Maglite D magnesium oxide powder from Calgon. The tensile strength increased to
 30 1703, 1683, 1690, 1677 and 1953 psi (11.74, 11.60, 11.65, 11.58 and 13.47 MPa) respectively for these dusting agents:

Example 19

35

A blend containing 34.0% of the acrylic elastomer used in Example 4, 16.0% of the polyester elastomer used in Example 4 and 50.0% of Charguard 329 flame-retardant filler was prepared, the percentages in weight thus totaling 100%. The blend was then modified to include 2% by weight of Naugard 445 antioxidant, 0.5% Irganox 1010, 0.5% DLTDP secondary antioxidant, 2.7% carbon black, and 0.14% VAROX
 40 curing agent. The blend when tested provided excellent mechanical properties, was flame-retardant and emitted low smoke when burned.

Example 20

45

A blend containing 50% of the ATH used in Example 4, 15% of a polyamide elastomer with a specific gravity of 1.01, melting point of 173°C and melt index of 3g/10min. at 325°C and 1kg with a 2mm die and elongation of 380%, and 35% of the ethylene-propylene-diene terpolymer elastomer used in Example 9 was prepared in a laboratory Banbury. The blend also contained 2% Naugard 445, 0.5% Irganox 1010, 0.5%
 50 DLTDP and 0.14% VAROX curing agent. The blend when tested gave excellent mechanical properties, was flame retardant and emitted low smoke when burned.

55

Example 21

A blend containing 50% of the ATH used in Example 4, 15% of the polyester elastomer used in Example 4 and 35% of another polyamide elastomer with specific gravity 1.01, melting point of 148°C, m It
 5 index of 9 g/10min. at 235°C and 1kg with a 2mm die and elongation of 715% was pr pared. The blend also contained 2% Naugard 445, 0.5% Irganox 1010 and 0.5% DLTDP. The blend when tested gave excellent mechanical properties, was flame-retardant and emitted low smoke when burned

10 **Claims**

1 A halogen-free thermoplastic elastomer composition comprising:

(A) a flame retardant halogen-free inorganic filler and

(B) at least two elastomers selected from the group consisting of ethylene-propylene copolymers and
 15 terpolymers, polyamides, polyesters, polyisobutylene, polyurethanes, acrylic polymers, natural rubber, polybutadiene, polyisoprene or a graft copolymer or block copolymer comprising polymer segments of at least two such elastomers,

in which composition the weight % of (A) is at least 50% of the total weight of (A) and (B).

2. A composition as claimed in claim 1 in which the inorganic filler is selected from the group
 20 comprising of hydrated magnesia, aluminium trihydrate, hydrated calcium silicate, clays, talc, carbonates, hydrates, oxides, other silicates, nitrogen/phosphorous compositions and mixtures thereof.

3. A composition as claimed in claim 1 or claim 2 in which the proportion of filler is in the range from 50 to 75% by weight.

4. A composition as claimed in any one of claims 1 to 3 in which in addition to components (A) and (B)
 25 the composition includes additives in an amount of not more than 15% by weight.

5. A composition as claimed in any one of claims 1 to 4 in which the ratio of the two selected elastomers varies from about 95:5 to 50:50 respectively in parts by weight.

6. A composition as claimed in any one of claims 1 to 5 which contains sufficient curing agent to convert the composition into a thermoset after processing into its final shape.

30 7. A composition as claimed in any one of claims 1 to 5 which contains an elastomeric curing agent in an amount which is from 1 to 90% of the amount necessary for a substantially complete cure.

8. A composition as claimed in any one of claims 1 to 7 in which the inorganic filler is hydrated magnesia and the two elastomers are an acrylic elastomer and an ethylene-propylene-diene elastomer.

9. A composition as claimed in any one of claims 1 to 7 in which the inorganic filler is aluminium
 35 trihydrate and the two elastomers are:

(i) an acrylic elastomer and a polyester elastomer

(ii) an ethylene-propylene-diene elastomer and a polyester elastomer,

(iii) a polyester elastomer and a polyamide elastomer or

(iv) a polyamide elastomer and an ethylene-propylene diene elastomer

40 10. A composition as claimed in any one of claims 1 to 5, or claims 7 to 8 in which the elastomers are partially crosslinked.

11. An article produced by moulding or extruding a composition as claimed in any one of claims 1 to 10.

12. A method for preparing a halogen-free thermoplastic elastomer composition comprising blending
 45 together

(A) a flame retardant halogen-free inorganic filler and

(B) at least two elastomers selected from the group consisting of ethylene-propylene copolymers and
 50 terpolymers, polyamides, polyesters, polyisobutylene, polyurethanes, acrylic polymers, natural rubber, polybutadiene, polyisoprene or a graft copolymer or block copolymer comprising polymer segments of at least two such elastomers,

the weight % of (A) being at least 50% of the total weight of (A) and (B).

13. A method as claimed in claim 12 in which the filler and elastomers are blended together with an elastomeric curing agent in an amount which is from 1 to 90% of the amount necessary for a substantially complete cure and dynamically partially crosslinking the blend.

55 14. A method as claimed in claim 12 in which the thermoplastic elastomer composition is at least partially crosslinked by irradiating the composition using high energy microwave or ultraviolet radiation.

15. A method as claimed in claim 12 in which the filler and elastomers are blended together with sufficient elastomeric curing agent to convert the composition into a thermoset, processing the composition into its final shape and then curing the composition to convert it into a thermoset.

16. A thermoset composition prepared by a method as claimed in claim 14 or claim 15.

5 17. A wire or cable having a flame retardant jacket which is an extrusion coated layer comprising (A) a flame retardant halogen-free inorganic filler and
(B) at least two elastomers selected from the group consisting of ethylene-propylene copolymers and terpolymers, polyamides, polyesters, polyisobutylene, polyurethanes, acrylic polymers, natural rubber, polybutadiene, polyisoprene or a graft copolymer or block copolymer comprising polymer segments of at
10 least two such elastomers,
in which composition the weight % of (A) is at least 50% of the total weight of (A) and (B)

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 31 1157

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL4)
X	EP-A-0 004 017 (AEG TELEFUNKEN KABELWERKE AG) * Claims; example II *	1-8,10-17	C 08 K 3/00 C 08 L 101/00 H 01 B 3/44 //
D,A	FR-A-2 387 262 (RAYCHEM LTD) * Claims; page 4, line 32 - page 5, line 32 *	1	(C 08 L 101/00 C 08 L 7:00 C 08 L 9:00 C 08 L 23:16 C 08 L 23:18 C 08 L 33:06 C 08 L 51:00 C 08 L 53:00 C 08 L 67:00 C 08 L 75:04 C 08 L 77:00)
A	GB-A-2 107 720 (RAYCHEM LTD) * Claims; example 1 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. CL4) C 08 K C 08 L
Place of search THE HAGUE		Date of completion of the search 11-03-1988	Examiner DE LOS ARCOS Y VELAZQUEZ
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			